This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Library
of the
University of Wisconsin

University of Wisconsin Library

Manuscript Theses

Unpublished theses submitted for the Master's and Doctor's degrees and deposited in the University of Wisconsin Library are open for inspection, but are to be used only with due regard to the rights of the authors. Bibliographical references may be noted, but passages may be copied only with the permission of the authors, and proper credit must be given in subsequent written or published work. Extensive copying or publication of the thesis in whole or in part requires also the consent of the Dean of the Graduate School of the University of Wisconsin.

This thesis by...
has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

A Library which borrows this thesis for use by its patrons is expected to secure the signature of each user.

NAME AND ADDRESS DATE

M3-J3

THE PENTAVALENCE OF BISMUTH

by

EDGAR BURTON HUTCHINS JR

A Thesis submitted for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF WISCONSIN

1903

398745
OCT -6 1933
AWM
.H97

THE PENTAVALENCE OF BISMUTH.

Introduction.

There is much disagreement as to the conditions necessary for the formation of the compounds of bismuth in which it has a valence of five. In fact there is no compound of pentavalent bismuth whose existence is not questioned in the literature. But few attempts have been made to prepare the pentahalides of bismuth. Bismuth falls, in the arrangement of the elements according to the natural system, in group five which contains phosphorus, arsenic and antimony. These elements all form well defined compounds in which they show a valence of five. The following are some of the types followed:-

PCl_5, H_3PO_4, HPO_3, $H_4P_2O_7$, P_2S_5 and P_2O_5.

The pentoxide is the best defined oxide of phosphorus. But antimony trioxide is much better defined than the pentoxide. In the series the pentoxides show more pronounced acidic properties than the trioxides. The acidic properties decrease with the increase of the atomic weight. If the compounds in which these elements show the valence of three are considered it will be noted that bismuth naturally follows antimony as the most positive element in the series phosphorus, arsenic, antimony, bismuth. Phosphorus forms the well defined phosphine which shows definite basic properties. Arsenic and antimony form compounds of this type. Stibine is poorly defined and shows no basic properties. Bismuth does not form a compound with hydrogen.

Phosphorus trichloride and arsenic trichloride when treated with water give respectively phosphorus acid and arsenious acid. Antimony trichloride gives $Sb\ O\ Cl$ with alcohol only while bismuth trichloride reacts with water to form the well defined compound $Bi\ O\ Cl$. Bismuth might form compounds of the types $Bi\ Cl_5$, $Bi_2\ O_5$, $H\ Bi\ O_3$ and $H_4\ Bi_2\ O_7$.

The following work has been undertaken with the object of determining what compounds of pentavalent bismuth if any, exist and under what conditions they exist.

BISMUTH PENTOXIDE AND ITS DERIVATIVES.

In 1818 Brandes and Buchholz (Schweigger's Jr.für Chem. und Phys. 22-27) prepared an oxide of bismuth containing more oxygen than the trioxide. Since that time many chemists have tried to prepare bismuth pentoxide, bismuthic acid and potassium bismuthate. Some investigators have described the preparation of these compounds without difficulty while others who have repeated the experiments have not been able to obtain the compounds. Arppe (Pogg. Ann. 64-37) describes both bismuthic oxide and bismuthic acid. He states that he prepared these compounds by passing chlorine gas into a concentrated solution of potassium hydrate in which bismuth trioxide was suspended. The method of preparation of $H\ Bi\ O_3$ differed from that of $Bi_2\ O_5$ only in the ratio between the amounts of alkali and trioxide used. In the case of $H\ Bi\ O_3$ a larger excess of the alkali was used. The

products were washed with dilute nitric acid. The other details of the experiments are not given. It is probable that his products were mixtures of $H Bi O_3$, $K Bi O_3$ and the lower oxides of bismuth.

Schrader (Liebig's Annalen 121-204) made several attempts to prepare bismuthic oxide by the method used by Arppe. He worked with both dilute and concentrated solutions of potassium hydrate. He did not obtain $H Bi O_3$ or $Bi_2 O_5$ in any of his experiments. When he washed his reaction products with concentrated nitric acid he obtained the very difficultly soluble $Bi_2 O_4 \cdot 2 H_2O$. If he used dilute nitric acid he always found potassium in the final product. Muir. (Jr. Chem. Soc. 39-22) describes bismuthic acid and bismuth pentoxide. He states that these compounds can be prepared without difficulty by passing chlorine into a hot concentrated solution of potassium hydrate containing bismuth trioxide until a homogeneous heavy chocolate-red powder is formed. In view of experiments described later as performed in this laboratory it is doubtful if these results can be readily obtained. Muir found a solution of potassium hydrate with a sp. gr. of 1.37 to give good results. He washed the dark red brown powder obtained in the above manner with hot water. It was then boiled for a short time with concentrated nitric acid when it changed to a scarlet red powder. It was then dried over sulphuric acid for several days. He states that this product

was $Bi_2O_5H_2O$. When heated to 120° for three hours it contained 83.87% of bismuth. (Bi_2O_5 requires 84%.) After the reaction products had been washed until they had no effect upon litmus paper they contained potassium in varying proportions. If the product is washed too long with concentrated nitric acid $Bi_2O_4 \cdot 2H_2O$ is formed. Muir states that if Bi_2O_5 is heated to 225° it breaks down to Bi_2O_4 and oxygen. If the temperature is raised to 305° Bi_2O_3 is formed. Muir states that $Bi_2O_5H_2O$ is not an acid as it does not form any salt. However, he has assigned a structural formula to $Bi_2O_5 \cdot H_2O$. He states that it may have a very weak acid reaction in the presence of a large excess of concentrated potassium hydrate.

Heintz (Pogg. Ann. 63-559) obtained red products by passing chlorine gas through a solution of potassium hydrate containing bismuth trioxide. He analyzed the products and found that they contained Bi_2O_5 besides water and potassium.

Hoffman (Liebig's annalen 223-110) passed chlorine into a cold solution of potassium hydrate (sp.gr. 1.54) containing suspended bismuth trioxide. He then added more of the alkaline solution and boiled. The product obtained was again suspended in potassium hydrate and the operation repeated. The products were red-brown to dark violet in color. They were of the type $X\,Bi_2O_5 \cdot Y\,KBiO_3$. A large number of formulas are given as representing the various products of his experiments. Hoffman

found that water containing carbon dioxide would remove nearly all of the potassium from his products. The final product obtained by boiling with concentrated nitric acid was $Bi_2O_4 \cdot 2H_2O$.

Andre (C.R. 114-359) states that $KBiO_3$ cannot be obtained but that the acid salts $4KBiO_3 \cdot 3HBiO_3$ and $KBiO_3 \cdot HBiO_3$ exist.

Deichler (Zeit. für anorg. Chem. 20-80) made a large number of experiments in which he passed chlorine gas into potassium hydrate containing Bi_2O_3. He varied the concentration, the temperature and the amount of excess of the alkali. He made complete analyses of his products and gives full data for all of his experiments. In no case did he obtain a homogeneous reaction product by this method. In all cases where he used a large excess of hot concentrated potassium hydrate solution he obtained mixtures of $KBiO_3$, $HBiO_3$ and the lower oxides of bismuth. He obtained $HBiO_3$ about 95% pure as a final product by using potassium hydrate with a sp.gr. of 1.39 to 1.5 and washing the reaction product for a short time with concentrated nitric acid. Upon washing the product for a longer time he obtained $Bi_2O_4\ 2H_2O$. By washing the reaction product with water at 0° and drying over sulphuric acid he obtained a product containing 13.9% potassium oxide; $KBiO_3$ requires 15.9%.

The experiments of Muir and Deichler have been repeated. In each case a very large excess of potassium hydrate was used. The products obtained varied in color from yellow to dark-chocolate. In most cases the product was a mixture of brown and red particles. In no case was it possible to obtain a homogeneous product. In one experiment ten grams of Bi O Cl was introduced into 425 C.C. of potassium hydrate (sp. gr. 1.43). chlorine was passed through the hot solution for three hours. The product obtained was washed with water at 0^{o} and dried over sulphuric acid. When dry the powder was dark red but it contained some particles of a bright red color. It contained much potassium. This powder was washed quickly with concentrated nitric acid and dried over sulphuric acid. It was then a bright red powder which appeared homogeneous. When exposed to the heat of the steam bath for a few hours it gradually assumed a chocolate color. All of the products prepared agreed in appearance with those described by Deichler.

In order to ascertain if a barium bismuthate can exist or if barium hydrate will retain any bismuthic acid chemically combined a series of experiments was conducted replacing the potassium hydrate in the previous work by barium hydrate. Chlorine was passed for several hours through a hot concentrated solution of barium hydrate containing solid Bi_2O_3. The bismuth was not oxidized to any appreciable extent.

Since caesium hydrate is the strongest base known it was thought that bismuth trioxide might be readily oxidized by chlorine in a hot concentrated solution of this base and perhaps a caesium bismuthate be formed. Two experiments were made to test this view. 20 grams of caesium hydrate was dissolved in a small amount of water. .5 grams of bismuth trioxide was introduced into the solution which was then heated. Chlorine was passed into the solution until it was saturated. The solution was acid at the close of the experiment. At no time during the experiment was any change evident. In the other experiment 4 grams of caesium hydrate and .3 grams of bismuth trioxide was used. In neither case was there any caesium in the yellow powder which remained after washing the product with hot water.

Bismuth trioxide can be oxidized to bismuth pentoxide by chlorine in a concentrated potassium hydrate solution. Bismuthic acid can be obtained in impure condition by washing the reaction product quickly in concentrated nitric acid. But the pure product has not been prepared in this manner. The reaction products are not homegeneous but may contain nearly as much potassium as is required by potassium bismuthate. The potassium can all be washed out with hot concentrated nitric acid. If the washing is continued for more than a few minutes the product is reduced to $Bi_2O_4 \, 2H_2O$.

Chlorine does not oxidize bismuth trioxide in a con-

centrated solution of barium hydrate.

Hasebroek (Ber. 20-213) states that he prepared bismuth pentoxide by the action of hydrogen peroxide on an acid solution of a bismuth salt. The acid was neutralized by the addition of ammonia. Lorch repeated this experiment obtaining a product similar in appearance to Hasebroek's bismuth pentoxide. His analysis showed it to consist almost wholly of $Bi_2 O_3$.

In order to test the action of hydrogen peroxide upon bismuth salts a series of experiments was performed. A solution of bismuth chloride in hydrochloric acid was treated with a large excess of H_2O_2. This mixture was then poured into a hot concentrated solution of potassium hydrate. A brown precipitate was formed immediately. This was washed with hot water. It was then found to dissolve readily in dilute nitric acid. Consequently was not bismuth pentoxide. In other experiments ammonia was substituted for potassium hydrate. But the precipitate formed was light yellow in color.

BISMUTHIC ACID BY ELECTROLYSIS.

In order to secure better conditions than can be obtained by passing chlorine into an alkaline solution Deichler (Zeit. für anorg. Chem. 20-103) electrolyzed a concentrated solution of potassium hydrate containing a little potassium chloride and solid bismuth trioxide. The bismuth trioxide was gradually converted into a heavy dark red powder. This product

was washed with water at ordinary temperatures. It was found that the amount of potassium in the product diminished slowly as the washing was continued. In order to obviate the decomposition of the potassium bismuthate Deichler washed some of the reaction product with alcohol and other portions with water at 0°. The material was dried over phosphorus pentoxide and sulphuric acid for eight saya, when Deichler found it to be potassium bismuthate containing nearly three per cent. of water. A portion of this potassium bismuthate was heated with water for eight days and dried as before. It still contained 2.5% potassium oxide. In this treatment it lost 1% of its weight in oxygen. Deichler obtained bismuthic acid about 95% pure by washing potassium bismuthate quickly with hot concentrated nitric acid. When heated to 120° the potassium bismuthate gradually assumed a black color. At 300° it lost two atoms of oxygen.

THE ACTION OF CHLORINE UPON BISMUTH TRICHLORIDE.

Since phosphorus, arsenic and antimony form well defined pentachlorides it was thought best to make some experiments to retermine whether or not bismuth forms a pentachloride. The simplest way to prepare such a compound would be to treat the trichloride with chlorine.

Muir (Jr. Chem. Soc. 1877-I-144) attempted to prepare bismuth pentachloride. He passed chlorine gas over fused bismuth trichloride. The crystals obtained in this manner melted

at 227° , the melting point of the trichloride. The product was therefore bismuth trichloride. Muir also heated to redness a mixture of bismuth oxychloride and powdered charcoal. After displacing the air by carbon dioxide he passed chlorine over the misture. The sublimate consisted of white crystals containing 33.5% chlorine. The product was bismuth trichloride. Muir fused together sulphur and bismuth trichloride. He obtained Bi S Cl and not Bi S Cl_3. He also treated $Bi_2 O_3$ with chlorine with a view of obtaining Bi O Cl_3 analogous to P O Cl_3 but the product was bismuth trichloride.

Rauter (Leibig's 270-251) states that he treated bismuth pentoxide with silicon telrachloride and obtained bismuth trichloride as a product.

To test the action of chlorine on bismuth trichloride at very low temperature the following experiment was performed. Some dry powdered bismuth trichloride and some of the clear arystals were placed in a tube. The tube was placed in a Dewar bulb containing liquid air. Chlorine was gas passed into the tube and at once assumed the solid state. When the tube was about one-half full of the solid chlorine it was withdrawn from the bulb and the chlorine melted. The trichloride of bismuth was then well shaken up with the liquid chlorine. The tube was returned to the liquid air where it was kept for an hour or more. The trichloride remained unchanged in appearance during the whole

course of the experiment. After the chlorine had evaporated analysis of the powdered material showed it to contain 33.2% of chlorine. From this experiment it is evident that bismuth pentachloride is not formed by the action of solid or liquid chlorine upon bismuth trichloride. Other similar experiments were made in which the bismuth trichloride was kept in contact with chlorine at—15° for several hours. In no case was the trichloride changed in appearance by the action of the chlorine upon it.

In order to determine whether or not bismuth pentoxide is attacked by hydrochloric acid at low temperature the following experiment was made. A small quantity of impure bismuth pentoxide was kept at a temperature below--10° while dilute hydrochloric acid was added to it. The pentoxide dissolved at that temperature with the evolution of chlorine gas.

THE ACTION OF CHLORINE UPON THE DOUBLE HALIDES OF BISMUTH.

A concentrated solution of bismuth trichloride in dilute hydrochloric acid was saturated with chlorine at --10°. Solid ammonium chloride was then added as long as it would dissolve. The solution was evaporated to crystallization over sulphuric acid. The colorless crystals were dried between filter papers and analyzed. They were found to contain 49.1% bismuth and 42.7% chlorine. The compound formed was therefore $2\,NH_4Cl \cdot BiCl_3$. This compound is described by Deherain

(Comp. Rend. 54-726). The chlorine was determined as silver chloride. The bismuth was weighed as bismuth sulphide.

Experiments were made with a view of obtaining a pentahalide of bismuth by the action of a perhalide of caesium upon a halide of bismuth. $CsICl_2$ was prepared as described by Wells & Penfield (Am. Jr. Sc. 43-27). To a hot concentrated solution of 1.4 grams of this perhalide 1.3 grams of bismuth trichloride in dilute hydrochloric acid was slowly added while chlorine was passed through the solution. At once a yellow crystalline precipitate formed. In one experiment the substance was dessolved in hydrochloric acid and recrystalized over sulphuric acid. Analysis showed it to contain 35.0% caesium, 37.0% bismuth and 27.8% chlorine. The compound was therefore 2 Bi Cl_3-3 Cs Cl. The bismuth was precipitated from a nitric acid solution by ammonicun carbonate and weighed as bismuth trioxide. The caesium was converted to caesium sulphate after the bismuth had been removed from the solution by hydrogen sulphide. This compound is described by Brigham (Am. Chem. Jr. 14-181).

To a hot solution of caesium tribromide a hydrobromic acid solution of bismuth tribromide and bromine was added. At once a finely divided yellow precipitate was thrown down. It was quite insoluble in hydrobromic acid but readily soluble in hydrochloric and nitric acids.

Analysis showed this compound to be a new salt cor-

responding to the formula $2\ Bi\ Br_3\ 3\ Cs\ Br$.

Wt salt	wt.	% found		% calculated.
0.1433	$Ag\ Br$ 0.1580	46.9-Ag	-	46.8
0.2400	$Bi\ O\ Cl$ 0.0835	27.9-Bi	-	27.1
0.2400	$Cs_2S\ O_4$ 0.0384	27.0-Cs	-	26.1

---------0-----------

SUMMARY.

Bismuth trioxide can be oxidized to the pentavalent condition by chlorine in a hot concentrated solution of potassium hydrate. By washing the reaction products quickly with concentrated nitric acid impure bismuthic acid is obtained. It is a very weak acid and is insoluble.

Potassium bismuthate is the only salt of bismuthic acid which has been isolated. It can be made by the electrolysis of a concentrated solution of potassium hydrate containing potassium chloride and bismuth trioxide. It is partially decomposed by washing with warm water yielding bismuthic acid.

No pentahalide of bismuth has been described. Bismuth trichloride is uneffected by solid, liquid and gaseous chlorine.

The perhalides of caesium do not oxidize the trihalides of bismuth to the pentavalent form. They react however, giving double salts of the type. $2\ Bi\ Cl_3\ 3\ Cs\ Cl$.

Approved June 1 1903

Victor Lenher

L. Kahlenberg.

89086032224

b89086032224a